



Catalytic hydrodechlorination of chlorobenzene over supported palladium catalyst in buffered medium

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ABSTRACT

The catalytic hydrodechlorination (HDC) reaction, which is an attractive abatement process for chlorinated organic wastes, was studied over a magnetically recoverable supported Pd(0) catalyst. We investigated the most favorable reaction conditions under which to obtain the highest substrate conversion rates while preserving the catalyst properties and morphology. Sodium hydroxide, triethylamine and buffered solutions were used as proton scavengers in the HDC of chlorobenzene under mild conditions. It was observed that sodium hydroxide caused corrosion of the silica support, triethylamine in 2-propanol preserved the morphology of the catalyst which could be recycled for up to five successive HDC reactions, and aqueous buffer solutions preserved the catalyst morphology and the catalytic activity for up to four successive HDC reactions. The use of buffer solutions to neutralize the HCl formed during the HDC reaction is an interesting, less aggressive, alternative approach to HDC reactions.

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1. Introduction

Chlorinated organic compounds are largely used as raw materials, intermediates and solvents in the chemical, agrochemical and pharmaceutical industries [1,2]. These compounds are known for their persistence in the environment and high toxicity, and have recently gained attention for their contribution to ozone layer depletion, the formation of acid rain and the greenhouse effect. Moreover, many of these compounds are mutagenic and carcinogenic [3–5]. The catalytic hydrodechlorination (HDC) of chlorinated aromatic wastes can be considered an environmentally friendly alternative to traditional disposal options which include incineration, pyrolysis, catalytic steam reforming, biological treatment, adsorption on charcoal, and catalytic oxidation (e.g., photocatalysis). All of these processes are associated with drawbacks like highly toxic emissions due to, for example, the formation of dioxins and furans [6]. The HDC reaction does not lead to complete degradation of the pollutant, however, it generates less toxic products that can be more easily biodegraded or even of commercial importance [6]. Many catalytic systems have been developed to perform and study the mechanism of the HDC process [7–10]. The major problem associated with this reaction is the deactivation of the catalyst which can be caused by halogen adsorption, modification of the catalyst surface or the formation of oligomers. In order to reduce the influ-

ence of the acid formed during the reaction, it is usually performed under basic conditions [11–13]. Different bases have been used as proton scavengers in various solvents for liquid-phase HDC reactions [10,14–17]. A variety of metal catalysts have been employed in HDC reactions, such as Pd [18–21], Pt [22], Rh [23], Ru [24] and Ni [10], although Pd catalysts have shown the best performance under mild conditions [25–27]. Alumina [28–30], activated carbon [7,16,31] and silica [2,32–34] are among the catalyst supports most commonly used in the HDC reaction. The use of strong basic conditions can change the morphology of the catalyst support or even dissolve it, and therefore the support and the base should be chosen with care. The use of NaOH has been cited by many authors as a good proton scavenger for the HDC reaction [1,14,35,36], however, a strong basic medium can attack the catalyst support. The use of buffered aqueous solutions represents a milder alternative, but has been much less exploited in HDC reactions [37]. Similarly, triethylamine has been used in organic media [16].

Here, we demonstrate the activity of a magnetically recoverable Pd(0) catalyst in the HDC reaction of chlorobenzene under mild conditions. We investigated the most favorable reaction conditions under which to obtain the highest substrate conversion rates while preserving the catalyst properties and morphology.

2. Materials and instrumentation

2.1. Preparation of the catalyst support

The catalyst support consists of silica-coated magnetite nanoparticles, named FFSi, and was prepared via a microemul-

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sion method as described in detail in our previous papers [38–40]. Typically, 89.2 g of polyoxyethylene(5) isooctylphenyl ether was dispersed in 1.4 L of cyclohexane in a 3 L round bottom flask. Then, 10 mL of a cyclohexane solution of oleic acid coated magnetite (40 mg/mL) were added. The mixture was mechanically stirred until it became transparent and 19 mL of ammonium hydroxide (29% aqueous solution) were added to form a reverse microemulsion. Finally, 15.4 mL of tetraethylorthosilicate (TEOS) was added. The solution was gently stirred for 16 h. The silica-coated magnetite core-shell composite, named FFSi, was precipitated with methanol, and collected by centrifugation at 7000 rpm for 20 min. After being washed with methanol and ethanol, the material was dried first at room temperature and then at 60 °C for 3 h in an oven. The yield of each preparation is about 1 g of FFSi.

Before the metal loading, the support was functionalized with amino groups using (3-aminopropyl)triethoxysilane to give a better dispersion of palladium nanoparticles as previously discussed [39,40]. Typically, 0.30 mL of 3-(aminopropyl)-triethoxysilane (APTES), dissolved in 30 mL of dried toluene, was added to 200 mg of FFSi under inert atmosphere. The solution was stirred for 2 h at room temperature. The amino-functionalized solid (FFSi-NH₂) was washed with toluene, magnetically collected, and dried at 100 °C for 20 h in an oven.

2.2. Preparation of the catalyst precursor

The palladium catalyst was prepared by adding 200 mg of the catalyst support FFSiNH₂ to 10 mL of an aqueous [PdCl₄]²⁻ solution (0.5 mg L⁻¹). The suspension was stirred at room temperature for 1 h and magnetically separated with a permanent magnet. The solid was washed 2 times with 4 mL of water and dried in a desiccator under vacuum for 12 h. The Pd content in the final solid was 2.8 wt.% as analyzed by ICP OES.

2.3. Preparation of the Pd(0) catalyst

Prior to all HDC reactions the catalyst was reduced by molecular hydrogen at 6 atm and 75 °C. The metal reduction was carried out in a modified Fischer–Porter glass reactor loaded with the catalyst precursor Pd²⁺-loaded support (200 mg, 0.05 mmol Pd) and cyclohexene (1.62 g, 20 mmol) under inert atmosphere. The reactor was connected to a pressurized H₂ tank via a gas regulator set at 6 atm and the pressure was maintained constant for the entire course of the reaction by leaving the reactor open to the H₂ supply tank. The reaction was conducted under magnetic stirring (700 rpm) and the temperature (75 °C) was maintained using an oil bath and a stirring hot plate connected to a digital controller (ETS-D4 IKA). The reduction of the Pd²⁺-precursor forms the active Pd(0) nanoparticle catalyst that hydrogenates the amount of cyclohexene present. The hydrogenation reaction can be followed by the fall in pressure in the H₂ tank monitored with a pressure transducer interfaced through a Novus Field Logger connected to a computer. The complete conversion of the substrate by our Pd(0) catalyst typically takes around 20 min. After this time, the Pd(0) catalyst, named FFSiNH₂Pd, was isolated by magnetic separation and dried under reduced pressure for TEM analysis and used in subsequent HDC reactions. The hydrogenation reaction attests the metal reduction and helps to check the reproducibility of each catalyst preparation batch.

2.4. Reaction procedure

All liquid-phase HDC reactions of chlorobenzene with molecular hydrogen were carried out under constant pressure in a modified Fischer–Porter glass reactor connected to a pressurized H₂ supply tank. The hydrogen pressure was maintained for the entire course of the reaction by leaving the reactor connected to the H₂ gas supply

through a gas regulator set to the desired pressure of each experiment. In a typical HDC reaction, 50 mg of supported Pd catalyst FFSiNH₂Pd (0.013 mmol Pd), 3 mmol of chlorobenzene, 10 mL of solvent (or buffer solution) and the desired quantity of base were added to the reactor. The reactor was evacuated and attached to the hydrogenation apparatus. The reaction was conducted under magnetic stirring (700 rpm) at the desired pressure and temperature. The temperature was maintained constant using an oil bath and a stirring hot plate connected to a digital temperature controller (ETS-D4 IKA). After the desired time interval, the catalyst was recovered magnetically by placing a magnet on the reactor wall and the products were collected and analyzed by gas chromatography. Substrate conversions were calculated using response factors determined through standards. The buffered solutions used in the HDC reactions were prepared as follows: (a) acetate buffer: glacial acetic acid was added to a solution of sodium acetate (3.3 mol L⁻¹) until the pH reaches 6, (b) phosphate buffer: a solution of KH₂PO₄ (2 mol L⁻¹) was added to a solution of K₂HPO₄ (2 mol L⁻¹) until the pH reaches 8, (c) carbonate buffer: a solution of NaHCO₃ (2 mol L⁻¹) was added to a solution of Na₂CO₃ (2 mol L⁻¹) until the pH reaches 10.

2.5. Characterization methods

Transmission electron microscopy (TEM) analysis was performed on a Philips CM 200 operating at an accelerating voltage of 200 kV. The samples for TEM were prepared by collecting the nanoparticles dispersed in aqueous solution on a carbon-coated copper grid.

Gas chromatography analysis was performed on a Shimadzu GC 17A instrument equipped with a 30 m DB5 capillary column using the following parameters: isotherm 40 °C, injector temperature 150 °C, detector temperature 150 °C, and injection volume 1 µL.

3. Results and discussion

The magnetically recoverable Pd catalyst used in this study was obtained following the previously reported procedures for the preparation of the catalyst support [38] and a modification of the previously reported procedures for the preparation of supported Pd nanoparticles [40]. The catalyst support consists of silica-coated magnetite nanoparticles and shows excellent magnetic properties to allow magnetic separation, as reported previously [41]. The material responds to an external magnetic field due to the high saturation magnetization at room temperature (MS = 69 emu g⁻¹ of Fe₃O₄ at 70 kOe) and it does not remain magnetized when the magnetic field is removed (negligible coercivity field at room temperature). These magnetic properties allow a fast separation of the catalyst from the reaction media and easy redispersion for washing and use in successive reactions. All of these procedures can be carried out with the catalyst inside the reactor, which greatly minimizes the use of auxiliary substances and solvents, catalyst losses, catalyst oxidation by exposure to air, and time-consumption in laborious filtration procedures, among other factors.

Preliminary studies on the activity of the supported Pd catalyst led to very interesting results for the hydrogenation of cyclohexene, and also the role of different functional groups on the surfaces of the catalyst support [40]. Amino- and ethylenediamino-functionalized supports formed Pd(0) nanoparticles of ca. 6 and 1 nm, respectively. However, the catalyst comprised of small Pd(0) nanoparticles (ca. 1 nm) is less active than the catalyst comprised of ca. 6 nm Pd(0) nanoparticles. The latter hydrogenated cyclohexene with an average TOF of 5500 h⁻¹ and total TON of 50,000 mol_{substrate}/mol_{catalyst}

Table 1
HDC of chlorobenzene (CB) by FFSiNH₂Pd in different solvents and bases.

Entry	CB (mmol)	Base/mmol	Solvent	Cat (mmol Pd)	mol _{CB} /mol _{Pd}	Time (h)	Conversion (%) ^a	TON ^b
1	15.0	NaOH/18.0	H ₂ O	0 ^c	0	24	0	–
2	15.0	None	H ₂ O	0.026	580	1	>99	580
3	1.0	NaOH/1.5	H ₂ O	0.005	200	1	90	180
4	1.0	NaOH/1.5	H ₂ O	0.005	200	2	>99	200
5	3.0	NaOH/4.5	H ₂ O	0.013	230	2	>99	230
6	3.0	NaOH/4.5	2-Propanol	0.013	230	6	17	42
7	3.0	Et ₃ N/3.6	H ₂ O	0.013	230	4	>99	230
8	3.0	Et ₃ N/3.6	MeOH	0.013	230	4	>99	230
9	3.0	Et ₃ N/3.6	2-Propanol	0.013	230	4	>99	230
10	15.0 ^d	Et ₃ N/18.0	None	0.015	1000	6	55	550

Reaction conditions: solvent 10 mL; 75 °C, H₂ at 6 atm.

^a Determined by GC.

^b mol of substrate converted per mol of catalyst.

^c 100 mg FFSi (catalyst support).

^d More substrate was necessary to operate in solventless conditions.

after 20 successive runs of 2500 turnovers each at 75 °C and 6 atm of H₂ [40].

The present study deals with the performance of this Pd(0) catalyst in the catalytic hydrodechlorination (HDC) reaction, which is an attractive abatement process for chlorinated organic wastes. Chlorobenzene is often used as a model substrate for catalytic HDC studies because benzene is a main product of the reaction, unlike the polychlorinated compounds that can generate several intermediates, and for its presence in contaminated effluents [8,9,19,35,42]. The catalytic reactions were carried out under mild conditions in a modified Fischer–Porter glass reactor connected to a pressurized hydrogen gas tank. The Fischer–Porter bottle was set at a constant pressure for the entire course of the reaction by leaving it connected to the hydrogen supply through a gas regulator set at the desired pressure. After the desired reaction time the catalyst was recovered magnetically and the organic phase containing products was analyzed by GC. The conditions used and the conversion achieved in the catalytic HDC of chlorobenzene using the Pd(0) catalyst are summarized in Table 1. The catalyst support without Pd was tested as a blank experiment and no conversion was observed after 24 h (Table 1, entry 1). In all experiments in the presence of palladium (FFSiNH₂Pd), benzene was found as the only product as it was not further hydrogenated to cyclohexane. The catalytic HDC reaction of chlorobenzene proceeded to >99% conversion in aqueous medium even in the absence of base (Table 1, entry 2), however, the HCl formed (pH in the post-reaction solution <1) attacked the catalyst which could not be separated magnetically at the end of the reaction. In the presence of aqueous NaOH, high conversion was achieved in 2 h of reaction under mild conditions (Table 1, entry 4), and the catalyst could be magnetically separated from the reaction product. The recovered catalyst was recycled by adding new amounts of chlorobenzene and NaOH aqueous solution to the magnetically recovered solid, but the conversion of chlorobenzene decreased to 46%. The HDC reaction of chlorobenzene in the presence of aqueous NaOH was also complete (>99% conversion in 3 h of reaction) under milder conditions, such as lower pressure (H₂ at 1 atm) or lower temperature (50 °C), while keeping other reaction parameters as in Table 1 (entry 4). However, reducing the temperature to 25 °C (H₂ at 6 atm) caused a decrease in the chlorobenzene conversion to 70%. The HDC reaction in the presence of NaOH and alcohol resulted in lower conversion of chlorobenzene under similar reaction conditions (Table 1, entry 6). The HDC reaction using the palladium catalyst and triethylamine as a base in different solvents, such as 2-propanol, water and methanol, resulted in >99% conversion of chlorobenzene in all cases (Table 1, entries 7–9). The highest TON was achieved in the solventless reaction (Table 1, entry 10), but the conversion was 55% in 6 h and the purification was also more difficult because of the solid triethylammonium salt formed.

The presence of water helps the solubilization of the triethylammonium salt formed during the reaction, but the recycled catalyst lost its activity in the third cycle. On the other hand, the catalyst was active for up to 5 recycles in 2-propanol, as shown in Fig. 1. Sajiki et al. [43] have also reported good results using methanol as the solvent for the HDC of polychlorinated biphenyls with Pd/C. However, their catalyst does not work in aqueous medium.

The FFSiNH₂Pd catalyst was analyzed by TEM before (Fig. 2a) and after (Fig. 2b and c) the HDC reaction. As can be seen in Fig. 2b, the catalyst support was severely attacked by the strong basic aqueous NaOH medium (conditions of entry 4, Table 1) and corrosion of the silica layer can be observed. This can be the main reason for catalyst deactivation upon recycling. The spherical morphology of the support was maintained when Et₃N was used as the base in 2-propanol (conditions of entry 9, Table 1), although aggregation of the Pd(0) nanoparticles was revealed in the TEM image of the spent catalyst (Fig. 2c).

Considering that our HDC catalyst operates in aqueous medium and the presence of base is needed only to remove the HCl formed, we tested the catalytic HDC of chlorobenzene in buffered medium. When aqueous buffer solutions were used, the HCl formed during the HDC reaction was neutralized (pH was checked before and after the reaction) and the catalyst morphology was not severely affected during the reaction. Fig. 3 shows the TEM images of the spent catalyst isolated after HDC of chlorobenzene in aqueous

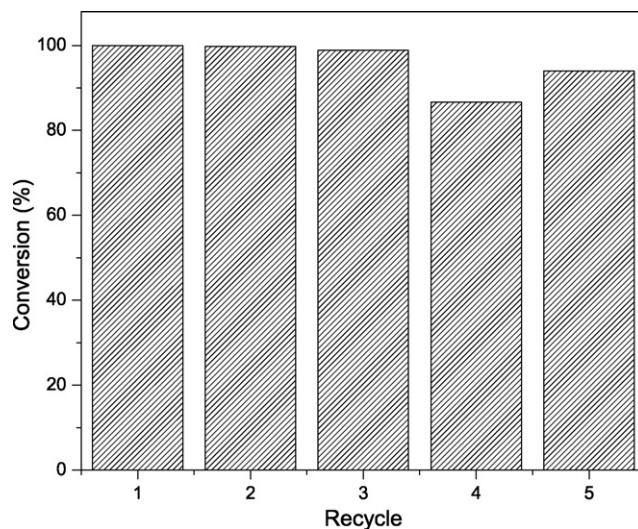


Fig. 1. Successive HDC of chlorobenzene by supported FFSiNH₂Pd catalyst. Reaction conditions: 3 mmol of chlorobenzene, 3.6 mmol of Et₃N, 10 mL of 2-propanol, 50 mg of supported catalyst (230 mol of substrate/mol of catalyst), 75 °C, H₂ at 6 atm.

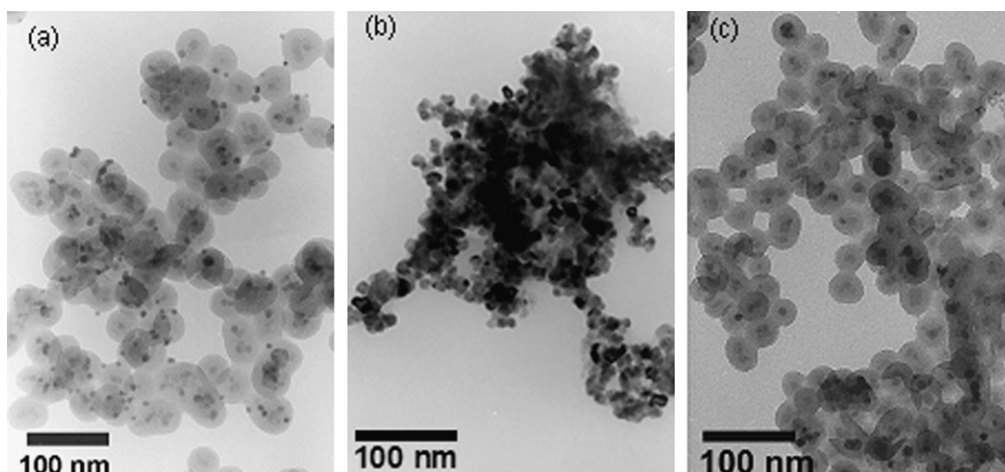


Fig. 2. TEM image of catalyst: (a) before the HDC reaction, (b) after the HDC reaction in NaOH/H₂O, and (c) after the HDC reaction in Et₃N/2-propanol.

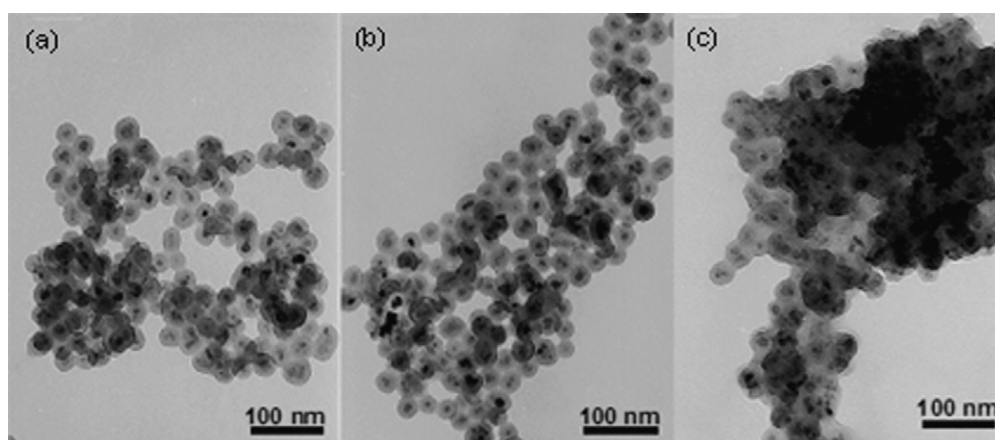


Fig. 3. TEM image of the spent catalyst after HDC reaction in (a) carbonate, (b) acetate and (c) phosphate buffered solutions. Reaction conditions: 3 mmol of chlorobenzene, 10 mL of buffer solution, 50 mg of supported catalyst (230 mol of substrate/mol of catalyst), H₂ at 8 atm, room temperature.

carbonate, acetate, and phosphate buffered medium, respectively. Table 2 summarizes the conversions obtained in the catalytic HDC of chlorobenzene in different buffer solutions with FFSiNH₂Pd. The phosphate buffer solution caused catalyst aggregation and the lowest conversion of chlorobenzene even after 24 h of reaction (~40% conversion). The acetate buffer preserved the morphology of the catalyst support and the complete conversion of chlorobenzene was attained in 17 h.

Table 2
HDC of chlorobenzene by FFSiNH₂Pd in buffered medium.

Entry	Buffer	Time (h)	Conversion (%)
1	Acetate (pH ~ 6) ^a	5	26
		8	51
		17	100
2	Carbonate (pH ~ 8) ^a	7	33
		10	67
		24	100
3	Phosphate (pH ~ 10) ^a	8	2
		16	10
		24	43

Reaction conditions: 3 mmol of chlorobenzene; 10 mL of buffer solution, 50 mg of supported catalyst (230 mol of substrate/mol of catalyst); H₂ at 8 atm, room temperature.

^a pH of the aqueous phase before and after the HDC reaction.

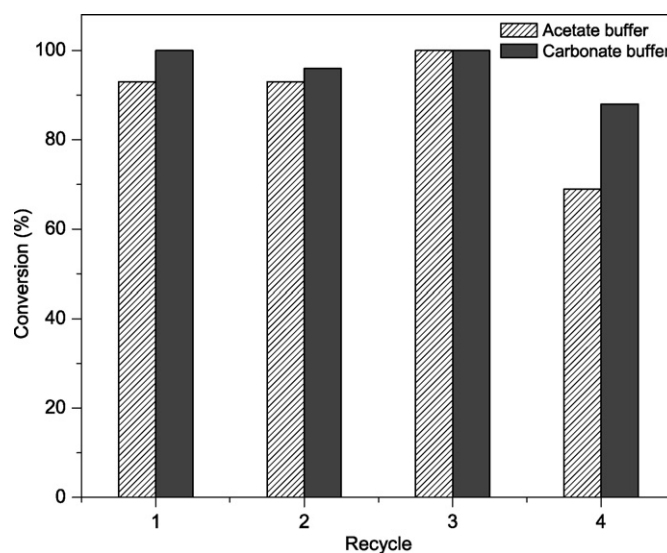


Fig. 4. Successive catalytic HDC of chlorobenzene by supported Pd(0) catalyst FFSiNH₂Pd in acetate (hatched) and carbonate (black) buffer solutions. Conditions: 3 mmol of chlorobenzene, 10 mL of buffer solution, 50 mg of supported catalyst (230 mol of substrate/mol of catalyst), H₂ at 8 atm, room temperature.

From the results of Fig. 3, it can be noted that both acetate and carbonate buffer solutions preserved the morphology of the catalyst support during the reaction and thus these catalytic systems are potential candidates for recycling tests. The recovered catalyst could be reused by adding new amounts of chlorobenzene and buffer solution to the magnetically recovered solid. The conversion of chlorobenzene (3 mmol each run) was maintained for three repeated cycles and a slight decrease in the conversion was observed only in the fourth run using the same catalyst sample (no fresh catalyst was added), as shown in Fig. 4. This means that turnovers of 1343 and 816 mol of substrate per mol of catalyst could be achieved in acetate and carbonate buffer, respectively, and the catalyst is still active in both media.

The supernatant solution, obtained after the catalyst was separated magnetically, was analyzed by ICP OES in order to check for the presence of leaching Pd and Fe ions. Metal leaching was negligible in most of the catalytic system used in this study. Even when NaOH was used as the base, the amount of palladium found was 7 ppm, which corresponds to only 0.028 wt.% of the palladium initially present in the support. The leaching of Fe was also very low, that is, 0.007 wt.% of the amount of Fe contained in the support.

4. Conclusions

In summary, our magnetically recoverable Pd(0) catalyst was found to show very interesting catalytic activity in the HDC of chlorobenzene. Sodium hydroxide, triethylamine and buffered solutions were studied as proton scavengers in the HDC of chlorobenzene under mild conditions. The use of aqueous sodium hydroxide solutions allowed complete conversion of the substrate in 2 h (TON = 230 mol/mol), but caused corrosion of the silica layer that protects the magnetic nanoparticles. Triethylamine in 2-propanol preserved the morphology of the catalyst which could be recycled for up to five successive HDC reactions with complete conversion of chlorobenzene in 4 h (TON = 230 mol/mol each run). In aqueous buffer solutions (acetate and carbonate) the catalyst morphology was also preserved and the catalyst activity was maintained for up to four successive HDC reactions. The use of buffer solutions to neutralize the HCl formed during the HDC reaction is an interesting, less aggressive, alternative, but still not well investigated in HDC reactions. Other important features provided by the catalyst are: (i) easy catalyst recovery by simply applying an external magnetic field; (ii) complete conversion of chlorobenzene to benzene under mild reaction conditions; (iii) HDC reaction performed in neutral aqueous medium; (iv) possibility of reusing the catalyst in successive reactions; and (v) negligible leaching of Pd and Fe into the products. Thus, the properties exhibited by the Pd(0) catalyst indicate that it has potential application in an efficient green recycling process for the catalytic HDC reaction of chlorinated organic compounds present in waste streams.

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